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(54) Title: METHOD AND USE OF A METHOD FOR THE DRY APPLICATION OF BARRIER AND ADHESIVE MATERIALS ON WEBS

(57) Abstract: The invention relates to dry polymeric materials, especially to dry materials useful as barrier or adhesive materials in dry-application onto a surface, such as polymer film, aluminium foil or the like and especially onto a moving web. The invention particularly relates to dry-application of barrier polymers and/or lamination adherents onto a web. In the method for the dry-application of barrier and/or adhesive materials onto webs or surfaces powdery polymeric material with particle or particle agglomerate size between 0.01 and 500 µm, preferable between 1 and 50 µm is dry-applied by ionic blasting onto a web or a surface, which is selected from paper, board, polymer film, metal foil, and which is optionally a moving web.

Method and use of a method for the dry application of barrier and adhesive materials on webs

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The present invention relates to dry polymeric materials, especially to dry materials useful as barrier or adhesive materials in dry-application onto a surface, such as polymer film, aluminium foil or the like and especially onto a moving web. The invention particularly relates to dry-application of barrier polymers and/or lamination adherents onto a web.

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Barrier polymers are widely used in packaging materials to avoid or decrease the penetration of water vapour, fat, odours, microbes, etc. through packages. As very few materials stop the penetration of all these media, multilayer structures are often needed. The manufacture of barrier layers is usually performed by extrusion of thermoplastic materials, such as variations of polyethylene and polypropylene, but also by dispersion coating. In the extrusion method, the required polymers are molten and applied onto the web through a slit as a thin film. The hot film adheres to the web mechanically, or in some cases, by means of an adherent material earlier applied to the web. One major disadvantage of this method is that the polymer material has to be heated until it is completely molten and then it is forced through the slit. Both the heat and the mechanical force (shear stress) lead to the breakdown of the polymer structure, causing decrease in mechanical properties, and sometimes decomposition. In the dispersion coating method, solvents or other liquid media are used, which require drying steps and consume energy.

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Same methods used for the application of barrier polymers onto a web are used for introduction of adherents, needed in lamination, onto webs. In the manufacture of multi-layer laminates, after coating with the adherent the webs are forced together by mechanical means with or without subsequent heating.

Based on the above it can be realised that there exists a need for an improved method for the manufacture of materials, especially packaging materials and laminates comprising one or several layers of barrier polymers.

5 The preparation of dry hollow or solid pigments or pigment granulates composed of several different materials used in paper and board coating has been described in *patent application FI-991438*. A water dispersion of pigments or a mixture of pigments and other material used for paper coating was spray-dried to a powder with a dry content of 85-100 %.

10 The use of such a plastic pigment powder, comprising agglomerates with a particle size of 1-500 μm , for dry-application onto paper and board webs, and a method for the dry-application has further been described in *patent application FI-991742*. In this dry-application method the powder is applied to the web by
15 means of an electrostatic field and then fixed to the web by heat. The prerequisite for this application method is that the powder is dry (dry content 85-100 %) and fine. A narrow particle size distribution contributes to the even result. The particles become electrically charged by corona treatment and/or by interacting with each other during transportation towards the web. The charged particles stick
20 to the web and stay there until fixation. Paper and board with improved quality are obtained by using this method.

An object of the invention is a method for the dry-application of barrier and/or adhesive material(s) onto a surface or a web.

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A further object of the invention is a method for the manufacture of materials, especially packaging materials and laminates, comprising one or several layers of barrier polymers.

A further object of the invention is the use of a dry-application method based on ionic blasting for the application of barrier and/or adhesive material(s) onto a surface or a web.

5 The characteristic features of the method for the dry-application of barrier and/or adhesive materials onto surfaces or webs, of the method for the manufacture of materials, especially packaging materials and laminates, comprising one or several layers of barrier polymers, and of the use of a dry-application method based on ionic blasting for the application of barrier and/or adhesive material(s) onto a web
10 or a surface are stated in the claims.

In the present invention it was discovered that paper, board, polymer film, metal foil or other surface or web, optionally a moving web may be coated by using a dry-application method with barrier and/or adhesive materials applicable in dry
15 form.

In the dry-application method small particles are applied onto a web or a surface without contacting it, by means of ionic blasting provided by high voltage, wherein the particles are charged by the ions formed by corona discharge.
20 Thereafter, an electric field transfers the charged particles onto the web or the surface.

Suitable barrier and adhesive materials are polymeric materials, such as polyethylene, polypropylene, ethyl vinylacetate, polyvinyl alcohols, polyamides,
25 ionomeres, copolymers of vinylidene chloride and methyl acrylate and the like, which are frequently used in extrusion applications, and thermoplastic biodegradable polymers, such as polylactides, polyglycolides and their copolymers.

30 Other suitable polymeric materials are polymers based on polystyrene, polyacrylate, polymethacrylate, poly(styrene-acrylate)copolymers, plastic

pigments based on melamin-formaldehyde and urea-formaldehyde or combinations thereof. If the polymeric materials are supplied as aqueous dispersions they must be dried before the dry-application. This procedure is described in *patent applications FI-991438 and FI-991742*.

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The essential features of the polymers in the dry-application method are particle size, glass transition temperature (T_g) and electrostatic properties. The typical diameter size of the particles, or particle agglomerates, is between 0.01 and 500 μm , preferable between 1 and 50 μm . In the case the material is supplied in the form of pellets, it must be ground, optionally with dry ice, to a powder with suitable particle size. The glass transition temperature (T_g) is preferably more than 40°, depending on the surface or web material used and on characteristics of the polymer. The polymer shall either be grindable or dryable and often a grinder is used in connection with application.

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The barrier and/or adhesive material i.e. the polymer powder is applied onto the web or the surface, which can optionally be a moving web, by using the dry-application method based on ionic blasting. The web or surface is selected from paper, board, polymeric film, metal foils such as aluminium foil, or the like. If the applied layer is to be the surface of a product and it is intended to be left uncovered, the powder layer may be covered with a film (polyethylene terephthalate or other non-sticking material) to avoid potential sticking of the polymer material to the surface of the calender rolls during fixing. The fixing is performed at temperatures suitable for the powder material, depending on nip pressure and calender speed.

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The method according to the invention has several advantages over the state of the art. The degrading effect of thermo-mechanical treatment on the polymeric material is decreased. By using the dry-application method it is possible to introduce materials with good barrier properties but which are too sensitive to thermal degradation or in other ways difficult to be utilised by conventional

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extrusion coating methods. Such materials are for example thermoplastic biodegradable polymers, such as polylactides, polyglycolides and their copolymers.

- 5 The dry-application methods allows the introduction of the adhesive layer in the lamination process without solvents or other liquid media, thus avoiding drying steps and saving energy.

10 The dry-application method allows one or more layers of one or different polymers to be applied before fixation. Also the thickness of the applied dry layer can be varied starting from very thin ($< 1 \text{ g/m}^2$) layers. The fixing parameters, such as characteristics of the powder material, temperature, nip pressure and calender speed will define the upper limit for each product.

- 15 The invention is illustrated in more detail in the following examples, which, however, are not intended to limit the scope of the invention.

Examples

- 20 The base materials chosen for the experiments where webs of paper ($81,4 \text{ g/m}^2$), PET-film (17.0 g/m^2) and aluminium foil, but depending on the intended use any kind of web material can be used. The dry-application barrier and/or adhesive materials where chosen among materials used in paper coating and lamination, especially in extrusion applications. These materials are usually provided in the
- 25 form of pellets with a diameter of 1-2 mm, and the material must thus be grounded to a powder before application. The tests were made with powders produced with a laboratory grinder. To avoid sticking the pellets were fed into the grinder together with dry ice. This grinder had a 0.25 mm screen, resulting in that the biggest fraction of the polymer powder was 0.25 mm.

The powders were applied to the webs by a laboratory dry coating device. The feeding was kept constant in all trials (24 g/m^2). In the lamination trials a PET-film was applied upon the powder, and the structure was led through a hot calender nip for fixing. In the barrier trials the PET film was applied to avoid sticking of the polymer material to the surface of the calender rolls during fixing. Afterwards the film was discharged. The calender speed was kept constant in all trials (about 6 rpm, accounting for about 5 m/min web speed). Three temperature ranges were used, 150, 170 and 190°C , and three nip pressures, 50, 100 and 150 bar, corresponding to 12, 25 and 37 kN/m linear load, respectively.

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The produced structures were tested for grammage, thickness and pinholes. For some samples the water vapour transmission rate (WVTR) was measured, too. Additionally the lamination structures were tested for delamination. For all materials the applicability of the material upon the web and the appearance of the produced structure were visually assessed.

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Example 1:**Barrier coating of paper with polyethylene.**

Polyethylene powder with a particle size (diameter) below 0.25 mm was applied onto a paper web by using dry-application technique. The application of the polyethylene powder onto the paper was satisfying, however the coating amount varied much, from 12.1 to 26.0 g/m^2 , the average being 18.2 g/m^2 . The thickness varied between 19.6 and $25.1 \mu\text{m}$, average $22.6 \mu\text{m}$. The results are presented in Table 2. The variation in coating thickness was caused by unevenness of the powder, which also caused pinholes. All tested nip temperatures and pressures worked, giving good adhesion to paper, and bad adhesion to PET film or aluminium foil. Delamination was very easy. The water vapour transmission rate was best (lowest) for samples prepared at 190°C , approximately $145 \text{ g/m}^2/\text{day}$.

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Table 1. Grammage and thickness of raw materials

Webs	Grammage, g/m ²		Thickness, µm	
	Average	St dev	Average	St dev
Paper web	81,4	0,2	95,8	0,2
PET film	17,0	0,1	12,6	0,3

Table 2. Grammage and thickness of coatings and laminate layers

Coatings	Example no	Grammage, g/m ²		Thickness, µm	
		Average	St dev	Average	St dev
Polyethylene	1	18,2	6,3	22,6	2,7
Saran MA 119	2	20,0	4,4	16,4	3,3

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Example 2:**Lamination of PET film to paper using Saran MA 119.**

10 Saran MA 119, a copolymer of vinylidene chloride and methyl acrylate, was applied onto a paper web by using dry-application technique. The application of Saran was good and quite uniform as can be seen from Table 2. Due to the higher melting temperature of Saran a calender temperature of 190 °C was used at all three nip pressures. Adhesion to both paper and PET film was good, but there was no adhesion of Saran to aluminium foil. There were only a few pinholes in the

 15 paper/PET-laminate, at nip pressures 100 and 150 bar about 25 holes/m², but at low nip pressure (50 bar) no pinholes could be found. The PET film itself showed no pinholes. The water vapour transmission rate was 1.4 - 4.7 g/m²/day, decreasing with higher nip pressure.

Example 3:**Barrier coating/lamination of paper with polylactide.**

5 The polylactide sample was a non-commercial sample of poly(L-lactide) with a molecular weight of about 90 000 g/mole. The material was applied to the paper web using the dry-application technique. Uneven ground powder polylactide led to an uneven application result. The adhesion to paper and PET film was, however, good.

10 **Example 4:**

Lamination of PET film to paper with Superchlon HE-510.

15 Superchlon HE-505, a chlorinated polyethylene, was applied onto a paper web by using dry-application technique. The application of Superchlon was good and uniform. The material has a higher melting point than the other polymers used, and needed a calander temperature of at least 210 °C for melting. All three nip pressures were tried. The adhesion to both paper and PET film was good.

Claims

1. A method for the dry-application of barrier and/or adhesive materials onto webs or surfaces, **characterised** in that powdery polymeric material with particle
5 or particle agglomerate size between 0.01 and 500 μm , preferable between 1 and 50 μm is dry-applied by ionic blasting onto a web or a surface, which is selected from paper, board, polymer film, metal foil, and which is optionally a moving web.
- 10 2. A method according to claim 1, **characterised** in that the polymeric material is selected from the group comprising polyethylene, polypropylene, ethyl vinylacetate, polyvinyl alcohols, polyamides, ionomeres, polystyrene, polyacrylate, polymethacrylate, poly(styrene-acrylate)copolymers, thermoplastic biodegradable polymers such as polylactides, polyglycolides and their
15 copolymers, plastic pigments based on melamin-formaldehyde and urea-formaldehyde or combinations thereof and polyesters.
- 20 3. A method for the manufacture of packaging materials or laminates with barrier polymers, **characterised** in that powdery polymeric material with particle size between 0.01 and 500 μm , preferable between 1 and 50 μm is dry-applied by ionic blasting onto a web or a surface, which is selected from paper, board, polymer film and metal foil and which is optionally a moving web, followed with fixation with a calender.
- 25 4. A method for the manufacture of packaging materials or laminates with barrier polymers according to claim 3, **characterised** in that the polymeric material is selected from the group comprising polyethylene, polypropylene, ethyl vinylacetate, polyvinyl alcohols, polyamides, ionomeres, polystyrene, polyacrylate, polymethacrylate, poly(styrene-acrylate)copolymers, thermoplastic
30 biodegradable polymers, such as polylactides, polyglycolides and their

copolymers, plastic pigments based on melamin-formaldehyde and urea-formaldehyde or combinations thereof and polyesters.

5 5. A method for the manufacture of packaging materials or laminates with barrier polymers according to claim 3 or 4, **characterised** in that more than one layer comprising same or different polymers are applied on the web or the surface before fixation.

10 6. A method for the manufacture of packaging materials or laminates with barrier polymers according to any one of claims 3 - 5, **characterised** in that the surface of the applied layer is covered with a film comprising non-sticking material, before fixation.

15 7. Use of a dry-application method based on ionic blasting for the application of barrier and/or adhesive material(s) onto a web or a surface, **characterised** in that powdery polymeric material with particle size between 0.01 and 500 μm , preferable between 1 and 50 μm is dry-applied by ionic blasting onto a web or a surface, which is selected from paper, board, polymer film and metal foil, and which is optionally a moving web.

20 8. Use according to claim 7, **characterised** in that the polymeric material is selected from the group comprising polyethylene, polypropylene, ethyl vinylacetate, polyvinyl alcohols, polyamides, ionomeres, polystyrene, polyacrylate, polymethacrylate, poly(styrene-acrylate)copolymers, thermoplastic
25 biodegradable polymers, such as polylactides, polyglycolides and their copolymers, plastic pigments based on melamin-formaldehyde and urea-formaldehyde or combinations thereof and polyesters.

30 9. Use according to claim 7 or 8, **characterised** in that more than one layer comprising same or different polymers are applied on the web or the surface before fixation.

10. Use according to any one of claims 7 - 9, **characterised** in that the surface of the applied layer is covered with a film comprising non-sticking material before fixation.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 01/01059

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: B05D 1/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: B05D, B65D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI DATA, EPO-INTERNAL

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4296142 A (GANAPATHY VASUDEVAN ET AL), 20 October 1981 (20.10.81), column 3, line 58 - column 4, line 2; column 4, line 53 - column 5, line 4, figure 1, abstract	1-4,6-8,10
Y	abstract	5,9
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X	GB 1285551 A (BRITISH INDUSTRIAL PLASTICS LIMITED), 16 August 1972 (16.08.72), column 2, line 50 - line 70; column 4, line 80 - line 85; column 5, line 10 - line 23, abstract	1-4,6-8,10
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☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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- "A" document defining the general state of the art which is not considered to be of particular relevance
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INTERNATIONAL SEARCH REPORT

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PCT/FI 01/01059

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4027366 A (JOHN M. MILLAR ET AL), 7 June 1977 (07.06.77), column 2, line 38 - line 55; column 4, line 23 - line 35; column 7, line 25 - line 30, abstract --	5,9
A	US 5176755 A (SHERMAN E. WINKLE, SR ET AL), 5 January 1993 (05.01.93), column 2, line 23 - line 39; column 5, line 43 - line 48, abstract --	1-10
A	US 3919345 A (SANTOKH S. LABANA ET AL), 11 November 1975 (11.11.75), abstract -- -----	1-10